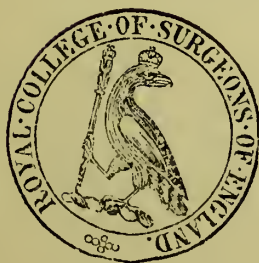


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ON
THE APPLICATION OF THE CONVERSION
OF
CHLORATES AND NITRATES INTO CHLORIDES,
AND
OF CHLORIDES INTO NITRATES,
TO
THE DETERMINATION OF SEVERAL EQUIVALENT NUMBERS.



BY
FREDERICK PENNY, Esq.

From the PHILOSOPHICAL TRANSACTIONS.—PART I. FOR 1839.

1839.

II. *On the Application of the Conversion of Chlorates and Nitrates into Chlorides, and of Chlorides into Nitrates, to the determination of several equivalent numbers.* By FREDERICK PENNY, Esq. Communicated by H. HENNELL, Esq. F.R.S.

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1. THE following researches originated from some experiments which were undertaken to discover an improved method for ascertaining the quantity of nitrate of potassa existing in crude saltpetre. After several unsuccessful attempts the action of hydrochloric acid was tried. The fact, that nitrates are decomposed by this acid, has been long known; but the nature of the resulting compound of potassium has not, so far as I am aware, been hitherto determined. I anticipated that the nitrate would be decomposed into chloride of potassium. To decide the question some pure nitrate of potassa was mixed with hydrochloric acid, and the mixture heated; while at common temperatures no perceptible action occurs, but immediately the acid becomes hot, decomposition commences. Chlorine and nitrous acid are evolved with copious effervescence, and the nitrate slowly disappears. The solution was gradually evaporated to dryness, and the dry salt treated with an additional quantity of acid until decomposition was no longer evident. The resulting salt was then carefully examined, and it was found to be pure chloride of potassium. This experiment was repeated several times, and all the results concurred in satisfactorily establishing the fact, that nitrate of potassa may be perfectly converted into chloride of potassium, provided a sufficient quantity of the acid be employed, and the temperature necessary to effect the decomposition be properly regulated.

2. So far the decomposition was admirably adapted for the object mentioned at the commencement. The usual impurities, such as chlorides, sulphates, silica, &c. which any sample of crude saltpetre might contain, would obviously remain unchanged, while the nitrate of potassa alone suffering decomposition, its quantity could easily be ascertained, by comparing the weight of the resulting salt with that obtained from a known quantity of absolutely pure nitrate. Several experiments were therefore performed to determine the exact quantity of chloride of potassium corresponding to a known weight of nitrate. The mean result of four experiments gave the ratio of 100 of nitrate to 73·730 chloride. I was then naturally led to compare this result with the equivalent numbers of these two compounds. In this country there are two series of equivalents in general use, one in which whole numbers are adopted, and the other in which fractional parts are admitted. For example, according to the former, nitrate of potassa will be 102, and to the latter 101·3. So chlo-

ride of potassium will be 76 and 74.6. Whence, according to the former, every 100 parts of nitrate should yield 74.51 of chloride: the latter gives the ratio of 100 to 73.613. But these results differ considerably from my experiments. In the one case, we have a difference of .78, and in the other .12. Whence therefore could they arise? Either the process must be defective, or the equivalent numbers, so generally considered as correct, must be erroneous.

3. To determine whether the process was inaccurate, I tried if chloride of potassium could be converted into nitrate of potassa by nitric acid. A single experiment upon some pure chloride decided in the affirmative; and the mean result of three experiments gave the ratio of 100 of nitrate to 73.727 of chloride. The correctness, therefore, of the experiments upon the nitrate was satisfactorily confirmed. Moreover in another experiment I converted a known weight of nitrate into chloride by hydrochloric acid, and then reconverted the resulting chloride into nitrate by nitric acid. The quantity of nitrate obtained was very nearly the same as that originally employed; there was not a hundredth of a grain difference. The error was thus traced to the equivalent numbers, but whether it existed in one, or more, of the elementary bodies constituting the above compounds, remained still unknown. The subject cannot be decided by the mere conversion of a nitrate into a chloride, or a chloride into a nitrate. Additional data are required. In order therefore to examine the question more scrupulously, the following experiments were undertaken; and as the results have proved consistent and satisfactory, I have presumed to submit them to the Royal Society.

4. In the present communication I propose to examine the equivalent numbers of oxygen, chlorine, nitrogen, potassium, sodium, and silver; and the following are the successive steps by which this examination has been conducted.

5. In the first place the equivalent of chloride of potassium will be determined, by decomposing the chlorate of potassa into oxygen, and chloride of potassium. From the ratio which these results bear to each other, the number for chloride of potassium, as compared with oxygen, may be easily deduced.

The same results will also give the number for chlorate of potassa.

Secondly. The equivalent of nitrate of potassa is ascertained. This is effected by converting the chlorate of potassa and the chloride of potassium into nitrate: and as we have already established the equivalents of chlorate and chloride, we can easily calculate the number for nitrate from these two methods of analysis. Moreover, from the equivalents of chlorate and nitrate of potassa, we can also learn the difference between the equivalents of chlorine and nitrogen, as the two salts agree exactly in composition, and only differ by nitrogen in the one being substituted for chlorine in the other. To confirm the experiments upon the conversion of chloride of potassium into nitrate, I have detailed some upon the decomposition of nitrate into chloride.

The process, hereafter described, by which these experiments were performed, was

so exceedingly simple, that the preceding differences could not be referable to errors of manipulation.

Thirdly. The equivalents of nitrate, chlorate, and chloride of sodium are resolved. The method of investigation is similar to that adopted for the analogous salts of potassium. The chlorate of soda has been decomposed into chloride, and into nitrate; the nitrate of soda into chloride; and the chloride of sodium into nitrate of soda. The results of all these experiments are perfectly consistent with each other, and they confirm in the most satisfactory manner the accuracy of the experiments upon the salts of potassium.

Fourthly. The equivalent numbers of chlorine, nitrogen, potassium, and sodium have been ascertained. For this purpose the metal silver has been selected. The salts of potassium or sodium do not admit of application in this respect, as it is impracticable to ascertain with sufficient accuracy for the present purpose, the proportions in which either of these metals combine with chlorine or nitric acid. Bismuth was first selected from the facility of converting it into oxide, but the difficulty of obtaining this metal in a state of absolute purity, and its liability to form subsalts, induced me to prefer silver. I have accordingly determined the exact proportions in which this metal combines with chlorine and nitric acid; and lastly, to prove the correctness of the relation which the resulting nitrate bears to the chloride, I have performed several experiments upon the conversion of the crystallized nitrate into chloride. Perfect consistency exists throughout; and from these results, conjoined with those from the salts of potassium and sodium, the equivalents of chlorine, nitrogen, potassium, sodium, and silver are easily deduced.

6. Such then is the arrangement of the evidence by which I propose to determine the equivalent numbers of these six elementary bodies; and to show that a slight alteration is necessary in those which are generally employed. Considering the number of distinguished chemists who have devoted their time and ability to the subject, it might naturally be expected that the truth had been satisfactorily established; but the slightest observation of the discrepancies in the results obtained, will prove the urgency of more refined investigations. In offering my feeble evidence, I am truly sensible of the responsible task I have undertaken. The well-attested skill of those from whom I shall have occasion to differ has constantly urged me to seek every means calculated to attain truth; and I trust, from the confirmatory nature of the evidence advanced, the numerous experiments performed, and the simplicity of the process employed, that the results will be entitled to confidence.

7. In presenting this communication, I beg to acknowledge, with sincere gratitude, the constant assistance I have received from Mr. HENNELL; he has kindly watched the whole progress of the investigations, and by his advice has enabled me to overcome several difficulties. Let it not, however, be inferred that he is responsible for any of the faults which this communication may contain: they must rest entirely on myself.

8. The violent effervescence which occurs during the action of nitric acid upon a

chloride, or of hydrochloric acid upon a nitrate, except in the case of silver, appeared, at first, to offer an insuperable difficulty to the application of these actions to so delicate a purpose as the determination of equivalent numbers. It was requisite that some simple practical method should be devised to obviate this source of error. The unavoidable loss occurring during effervescence has rendered many chemical processes, which promise the most favourable results in theory, inapplicable to important investigations. In the experiments hereafter to be described, any error from this cause has been effectually prevented. A loss by spiriting cannot occur. The substance is operated upon in a common flask placed in a horizontal position, with another attached to it as a receiver; the resulting substance is dried; and all the weighings are accomplished without removal from the flask. The performance and completion of the operation in one vessel is an additional advantage, and one which renders the process especially applicable to minute chemical researches. All those operations, such as transference, washing, filtering, &c. which introduce so many errors, are avoided. Little comment is required to show the advantages which the above process possesses in comparison to those hitherto applied to the determination of equivalent numbers. Few improvements, I imagine, can more increase the precision of our analyses, than a reduction of the number of operations by which these analyses are accomplished, combined with the employment of vessels which will bear a high temperature, resist the action of acids, and admit of being used with the most delicate balances. All these conditions have been fulfilled by the process employed in these researches, and as it has been applied to all the experiments, I shall premise its details thus early, to avoid unnecessary repetition.

9. Into a Florence flask, previously washed, dried, and tared, with the precautions hereafter stated, the substance to be operated upon was introduced, and its weight carefully ascertained. Another flask, with the whole of its neck removed, was also tared; and, as this was intended to be adapted to the other as a receiver, it was termed the receiver flask. The requisite quantity of acid was then poured upon the weighed substance, and the flask immediately placed in a horizontal position. The receiver flask was also adapted in the same position. If the decomposition would commence and continue without the assistance of heat, the flasks were allowed to remain as thus placed; but if heat were necessary, they were transferred without breaking the connection to a sand bath. The arrangement is represented in the accompanying figure, and from an inspection of this, it can readily be perceived that a

loss by spirting cannot occur. The drops of liquid, being ejected vertically by the effervescence, are thrown against the upper side of the flask. Should any drops be thrown laterally, a circumstance of rare occurrence, they will be secured by the receiver. When the decomposition is completed, and the action has entirely ceased, the receiver is detached, and the solution cautiously evaporated to dryness. The receiver in the meantime is dried and re-weighed. During the evaporation of the excess of acid, a portion of the vapour condenses upon the upper side of the flask, and, returning to the solution, carries with it any salt that may have been thrown to the top. Moreover, from this internal washing of the flask, as it may not inaptly be termed, continuing during the whole of the evaporation, the dry salt, instead of being scattered over a considerable portion of the flask, is reduced to a small compact mass. Indeed it is beautiful to observe the small compass which the dry nitrates occupy from this cause. The flask and its contents are lastly heated in the flame of a spirit lamp, and the dry salt either fused or not according to its nature. After a sufficient time has been allowed for the cooling of the flask, it is returned to the balance, and the weight of the resulting compound carefully ascertained.

10. From the preceding process it will be remarked, that flasks are the only vessels which have been employed. Many precautions must be observed to ensure their successful employment. Those that I have used are of the capacity of a pint, and the lightest were always selected. Their average weight was about 320 grains. Perfect cleanliness was obtained by boiling nitric acid, and well rinsing with common, and afterwards with distilled water. They were dried by heating on a sand bath, and then in the flame of a spirit lamp. I have found it advantageous to remove one half the necks; for by this, their weights are materially lessened, and their dryness is more securely ensured. While cooling they were placed inside a glass case, free from dust, and were allowed to remain for two hours, in order to restore the equilibrium of the internal and external air. In ascertaining the weights of the flasks, it is better to weigh them against another flask, previously selected and dried for the purpose. This latter flask may be termed the gauge flask. It weighed 323.420 grains, and weights were of course added, on either side, to adjust the difference between it and the flask to be tared. The gauge flask was frequently reheated to insure accuracy, and when not in use was preserved from dust and damp under a bell glass placed inside a glass case. Before the final observations of the weighings were noted, the flasks were allowed to remain in the balance for a quarter of an hour. The success of the operations depends especially upon a strict observance of these precautions. The following circumstance will serve as an ample proof of the care required. Having observed in one of the experiments a small particle of dust upon the flask, I removed it from the balance, and wiped it as quickly as possible once round with a silk pocket handkerchief. The flask was held during this operation by the very extremity of the neck. Upon returning it to the scale it had lost .025 of a grain, and this was owing to a slight expansion of the internal air, produced by the heat of the hand. It re-

gained its original weight in less than five minutes. By repeating this operation several times the flask lost nearly two tenths. The scales employed were made by Mr. ROBINSON, and would turn decidedly with the thousandth part of a grain, when loaded with five hundred grains. In the following experiments they were never loaded with so much. The weights were new, and by careful examination beforehand, were ascertained to be consistent.

Chlorate of Potassa.

11. It has already been stated, that the object with this salt, is its decomposition into oxygen and chloride of potassium. The method of accomplishing this hitherto has been to submit the salt to a high temperature; by which the oxygen is expelled and chloride of potassium remains. There are, however, many difficulties which render this process objectionable, and therefore I was induced to inquire whether the same result could be obtained by the action of hydrochloric acid. The changes occurring during the decomposition are well known. When the chlorate is in excess, the euclorine of SIR HUMPHRY DAVY, or, as since proved by SOUBEIRAN, a mixture of chlorine and chlorous acid, is evolved. If, however, the acid be in excess, chlorine only will be given off. All the oxygen of the chloric acid, and of the potassa, unites with the hydrogen of the hydrochloric acid, and forms water. The potassium remains combined with chlorine. I satisfied myself by numerous experiments that chloride of potassium is alone produced; and being enabled, by the process already described (9.), to counteract any error from the effervescence, I have adopted this method by hydrochloric acid in preference to that by heat.

12. The chlorate of potassa employed in the succeeding experiments was obtained pure by three successive crystallizations of ordinary commercial chlorate. After each crystallization the crystals were dried, rubbed to powder, and washed with distilled water. The salt which resulted from the third crystallization, dissolved without residue in water, and the solution was not affected by nitrate of silver or nitrate of baryta. Two hundred grains were converted by heat into chloride of potassium; the fused chloride was perfectly colourless, and when dissolved and tested not a trace of foreign matter could be detected.

13. The first experiments with this salt were rather discrepant, arising from my ignorance of the extreme caution which is requisite in drying it. Having observed in some chemical works that it is fusible at a temperature between 400° and 500° FAHR., and will bear a temperature of 660° without undergoing decomposition, I conceived that very careful fusion would be the most secure method for ensuring dryness. The want of uniformity in the results, however, indicated some source of error, and upon examination I found that a very notable quantity of chloride of potassium was produced by the process of fusion, although effected with the utmost care. A temperature just below that of fusion was next tried, but upon dissolving the dry salt in distilled water, and testing with nitrate of silver, a minute portion of chloride could

be detected. Indeed it was not until after several trials that I succeeded in ascertaining the temperature at which this salt might be perfectly dried without risk of decomposition. This temperature is about 220° . The temperature of boiling water is quite safe: 1000 grains were kept in a copper pan, heated by steam, for fourteen hours without experiencing the slightest change. I have found by several experiments that one hundred grains of perfectly dried chloride will lose about $\cdot 05$ of a grain by fusion. The precaution of testing a portion of the dry salt was repeated after every drying, to ensure accuracy.

14. When dry, the powder was transferred, while hot, into a small tube, and tightly corked. As soon as cold, the quantity necessary for an experiment was transferred into a previously tared flask, and the weight of it ascertained. The tube was sufficiently small to pass down the neck of the flask, and almost to the bottom, so that any adhesion of the powder to the sides of the flask was prevented. The remainder of the process corresponded to the one already described, except that before adding the hydrochloric acid, it is expedient to fuse the chlorate in the flask. By this the action is very much moderated, and the chlorate is slowly and quietly dissolved. No heat is requisite if the acid be sufficiently strong.

15. The hydrochloric acid was prepared according to the general directions in a green glass retort. It was twice re-distilled, and had a specific gravity of 1.160. It was carefully examined for sulphuric, nitric, and sulphurous acids, but not a trace of them could be detected. Two fluid ounces when evaporated left only $\cdot 015$ of a grain of solid matter*.

16. Owing to the compactness of the mass in which the resulting chloride is left in the flask, a minute portion of hydrochloric acid remains adherent to the salt when its quantity is large; and this cannot be driven off without so high a temperature as to risk the cracking of the flask. To expel this adventitious acid, I have always adopted the following process. The mass, the weight of which has been ascertained, is detached from the side of the flask by gentle agitation, and broken into pieces sufficiently small to be removed. These pieces are then rubbed to powder in a glass mortar, and the powder is transferred into a previously tared platina crucible. Its weight is ascertained, and then it is heated to dull redness for half an hour. Fusion was carefully avoided, as it cannot be effected without a minute loss by sublimation. When cold the loss is easily determined, and as the weight of the salt in the crucible is known, it is easy to calculate the loss for the whole quantity originally in the flask. The quantity which remained adherent to the flask generally amounted to $\cdot 07$ or $\cdot 08$ of a grain.

17. I subjoin the results of six experiments, and annex, for the convenience of comparison, the calculations to 100 parts.

* In the following experiments one fluid ounce of this acid was sufficient, so that not more than $\cdot 008$ of a grain of impurity would be introduced, and this quantity was always subtracted from the resulting chloride.

Chlorate.	Chloride.	Chlorate.	Chloride.
76.626 . . .	46.598 . . .	or as 100 to . . .	60.825
82.048 . . .	49.903 . . .	or as 100 to . . .	60.822
75.200 . . .	45.733 . . .	or as 100 to . . .	60.815
63.114 . , ,	38.386 . . ,	or as 100 to . . .	60.820
61.164 . . .	37.202 . . .	or as 100 to . . .	60.823
65.724 . . .	39.980 . . .	or as 100 to . . .	60.830

The mean of these experiments indicates that 100 parts of chlorate of potassa contain 60.823 of chloride of potassium, and 39.177 of oxygen.

18. In another experiment I obtained the proportion of 100 of chlorate to 60.808 of chloride; but in this case the chloride was partially fused, and while so I detected the evolution of a small quantity of white vapour. It shows that 60.808 is too low. **BERZELIUS** obtained by heat 60.850 of chloride, and 39.150 of oxygen from 100 of chlorate.

19. It being well known that many powders, although not deliquescent, are more or less hygrometric, and no precautions having been taken to obviate this in the preceding experiments, I thought an error on this account might influence them. To decide the query, the following experiment was performed. Two hundred grains of the chlorate in powder were dried with every care, and transferred while hot into a stoppered phial, just large enough to contain it. When quite cold, the stopper was removed for a moment, and then the bottle and its contents, being placed in a small glass dish, the whole was counterpoised in the balance. The powder was transferred very carefully into the dish, without removal from the balance, and the empty bottle placed on the top of the powder. The whole was left in this condition for two hours, and upon examination at the expiration of that time, not the slightest appreciable difference in weight could be detected. The experiment was twice repeated with the same result.

20. Perfectly dry powdered chloride of potassium was submitted to a similar experiment, but there was no evidence of change. If however the atmosphere be damp, both these salts when in powder rapidly absorb hygrometric moisture.

Conversion of Chlorate of Potassa into Nitrate.

21. Having determined, and I trust satisfactorily, that every 100 parts of chlorate correspond to 60.823 of chloride, the next object was to ascertain the quantity of nitrate resulting from 100 parts of the same salt. Its conversion into nitrate cannot however be performed directly, for the action of nitrate acid upon a chlorate, as I shall show at another opportunity, is not to decompose it wholly into nitrate, but into a definite mixture of nitrate and perchlorate. The means by which the object now desired was accomplished, were by converting the chlorate into chloride, by hydrochloric acid, and then the resulting chloride into nitrate, by nitric acid. The operations were performed without any removal from the flask. The nitric acid was

added immediately the chloride was dry, without transferring and driving off the small quantity of adhering acid (16.). The minuteness of its quantity rendered it of no importance, as considerable excess of nitric acid was always employed. The nitrate produced was always fused to ensure dryness, and its weight being ascertained, it was dissolved and tested for chlorate and chloride. There was never the slightest indication of either. The impurities introduced by the acids, namely, one ounce of hydrochloric, and half an ounce of nitric, were of course allowed for. Only four experiments were performed, as their uniformity assured me of their close approximation to the truth.

22. The particulars of them are as follows :

Chlorate.	Nitrate.	Chlorate.	Nitrate.
86.454	71.329	100	82.505
70.205	57.918	100	82.497
62.244	51.368	100	82.498
72.636	59.938	100	82.500

The mean will be as 100 chlorate to 82.500 of nitrate.

23. Hereafter I shall show that 100 parts of nitrate correspond to 73.726 of chloride, so that the above result would indicate that 100 of chlorate contain 60.825 of chloride. This agrees very closely with the experiments by hydrochloric acid.

24. Moreover, this result, by comparison with that obtained in 17, shows that
 100 parts of chloride correspond to 135.640 of nitrate.
 and 100 parts of nitrate correspond to 73.724 chloride.

Chloride of Potassium.

25 Notwithstanding the experiments which have been made upon the action of nitric acid upon chlorides, much uncertainty still exists, as to the precise nature of the changes which occur. Their explication would dispel the doubt respecting the changes which take place during the mutual decomposition of nitric and hydrochloric acid, in the formation of nitro-muriatic acid. Sir H. DAVY has stated that chlorine, nitrous acid, and water are produced. According to Dr. JOHN DAVY, a compound of chlorine and binoxide of nitrogen, with chlorine, and water result. Interesting as the decision of this question would be, I shall not now adduce the experiments I have made for this purpose, lest I should confuse the present inquiry. It has reference only to the ultimate result, which as before stated (3), is proved by the following experiment to be pure nitrate of potassa.

26. Two hundred grains of pure fused chloride of potassium were acted upon by one fluid ounce of nitric acid, sp gr. 1.425; effervescence began immediately on mixture: abundance of chlorine tinged with nitrous acid was evolved. After the action had continued for two hours, a gentle heat was applied. There was a more copious evolution of nitrous acid, but the action soon ceased, and the solution remained co-

lourless. Evaporation was carried to dryness, and the dry salt fused. It was colourless, and weighed about 271·24. This corresponds closely to the quantity of nitrate which should be yielded according to the preceding experiments. Part of the fused salt was then dissolved in distilled water, and tested with nitrate of silver: not the slightest turbidity was evident. To another portion hydrochloric acid was added, to observe whether any chlorate of potassa had been formed, but not the slightest change was produced. The remaining portion upon being crystallized proved to be all nitre.

27. The chloride employed was prepared by saturating pure bicarbonate of potassa with excess of pure hydrochloric acid. The bicarbonate was purified by three crystallizations, and when tested no indication of foreign matter could be detected. The solution of chloride was evaporated to dryness, and the dry salt heated to expel the excess of acid. It was then dissolved in distilled water, and twice recrystallized. The salt, thus purified, was examined for sulphate, nitrate, lime, &c., but no impurity could be discovered. It was dried by careful fusion in the platina crucible. The process has already been detailed. Only half a fluid ounce of the nitric acid was employed in the following experiments. This nitric acid had been twice distilled, and was perfectly colourless. It had a specific gravity 1·430. Two fluid ounces when evaporated left ·020 of a grain, and therefore not more than ·005 of a grain of impurity would be introduced.

28. The following are the particulars of the experiments performed:

Chloride.	Nitrate.	Chloride.	Nitrate.
84·090	113·058	100	135·639
61·998	84·092	100	135·637
51·823	70·293	100	135·640
67·145	91·072	100	135·635
55·350	75·071	100	135·630

whence, according to the mean,

100 of chloride correspond to 135·634 nitrate,
and 100 of nitrate correspond to 73·726 chloride.

29. In confirmation of these results, I procured some chloride from pure chlorate, by heating in the platina crucible, and fusing the resulting salt. I performed two experiments with this chloride and obtained the annexed results.

Chloride.	Nitrate.
38·660	52·438 100 135·640
60·998	82·732 100 135·630

They correspond very closely to the preceding.

Nitrate of Potassa.

30. The conversion of this salt into chloride of potassium has been described, as well as the process by which it is effected. In addition to the precautions mentioned

in the process, there are several others to be observed to ensure success. As soon as the action commences, the flask should be removed from the sand bath, and the decomposition be permitted to continue without heat. When the action slackens, the flask may be returned to the sand bath, and so on, to and from the source of heat, until it is so gentle that no lateral spirting can be feared. The adaptation of a receiver throughout the whole of these operations must be strictly attended to; for despite every care, a minute portion of the solution will sometimes be ejected during the evaporation. This circumstance happened in three of the experiments I shall mention presently. In one case the weight was $\cdot 003$ of a grain, in another $\cdot 008$, and in a third $\cdot 005$. The receiver flask should not be detached from the other even while removing them to and from the sand bath, nor in fact until the resulting chloride is nearly dry, as slight action continues during the greater part of the evaporation.

31. Very particular attention was paid to the purity of the salt employed. It was prepared from the common purified nitre of the shops, by four repeated crystallizations from distilled water. After each crystallization the salt was dried, and finely powdered, and this powder well washed with distilled water. When finally washed and dried, 200 grs. were fused in a platina crucible. They yielded a perfectly colourless mass, soluble in water without a trace of insoluble matter, and the solution was not affected by nitrate of silver, chloride of barium, oxalate of ammonia, or hydrosulphuret of ammonia. It was dried by careful fusion. The resulting chloride was dried in the same way as the chloride from chlorate. From one to two fluid ounces of hydrochloric acid are sufficient for the quantities of nitrate employed. In adding this acid one important practical circumstance must be observed, namely to add it in two successive portions, and to expel the first quantity previously to the addition of the second. This method is necessary from the small size of the flask, compared with the bulk of fluid. The less the quantity of fluid in the flask at one time, the less chance of loss by spirting.

32. I obtained, in seven experiments, the following very satisfactory results :

Nitrate.	Chloride.	Nitrate.	Chloride.
60.290	44.452	100	73.731
58.230	42.927	100	73.726
63.040	46.479	100	73.730
51.514	37.978	100	73.724
56.036	41.315	100	73.730
80.517	59.362	100	73.726
78.643	57.983	100	73.730

The mean will be as

100 of nitrate to 73.728 chloride,
or 100 of chloride to 135.634 nitrate.

33. Thus then we have ascertained, by three different methods, the ratio which chloride of potassium bears to nitrate of potassa. The results are as follows: from chlorate potassa (17.),

Nitrate.	Chloride.	Chloride.
100 corresponds to	73·724;	or 100 to 135·640

From chloride potassium (28.),

100 corresponds to 73·726; or 100 to 135·634.

From nitrate of potassa (32),

100 corresponds to 73·728; or 100 to 135·633.

Whence the mean will be,

100 corresponds to 73·726; or 100 to 135·636.

34. Before quitting this salt, I cannot omit the opportunity of mentioning an instructive circumstance connected with my first experiments. The hydrochloric acid employed was obtained pure (as I then thought) by the redistillation of some ordinary pure acid. It was tested for nitric and sulphuric acids, but there was not a trace of either. Two fluid ounces yielded by evaporation only ·014 of impurities. I performed four operations, and the results were in the ratio of 100 of nitrate of potassa to

73·877 . . 73·888 . . 73·886 . . 73·877 of chloride.

The close approximation of these numbers inspired considerable confidence at the time, and in order to verify them, I converted a portion of pure chloride of potassium into nitrate. The result was as 100 of nitrate to 73·728 chloride. The difference between this and the above result indicated some source of error. The chloride, resulting from a nitrate experiment, was therefore reconverted into nitrate by nitric acid, but instead of obtaining the original quantity, I obtained much less. This circumstance suggested, that the error arose from some impurity in the materials and suspecting the hydrochloric acid, a portion of it was submitted to another distillation. With this new acid another portion of nitre was decomposed, but the result was worse instead of better. The proportion was as 100 of nitrate to 74·04 of chloride. It was evident that some adventitious matter, more volatile than hydrochloric acid, was passing over with the acid in distillation. Sulphurous acid was suspected. A portion of the hydrochloric acid was boiled with a little nitric acid, diluted, and then tested with muriate of baryta; a precipitate of sulphate of baryta deposited. Therefore the acid did contain sulphurous acid, and this, by the action of nitric acid or a nitrate, was converted into sulphuric. The production of a higher result is therefore explained, and although vexatious at the time, it will now show the importance of obtaining the same result from different sources, and how admirably these reciprocal decompositions, of chlorides into nitrates and nitrates into chlorides, are adapted for this purpose.

Chlorate of Soda.

35 This salt has been very imperfectly examined. It is recommended to be prepared by passing chlorine through a solution of soda, and separating the chlorate and chloride by crystallization, or by saturating chloric acid with carbonate of soda. These processes, however, are very uncertain, and this may explain the contradictory descriptions given of this salt in chemical works. The process by which I succeeded in obtaining it pure, is as follows : some bitartrate of soda was prepared from carbonate of soda and tartaric acid, and purified by recrystallization. A quantity of pure chlorate of potassa was dissolved in a sufficient quantity of hot distilled water, and this solution while warm was mixed with a saturated hot solution of the above bitartrate of soda. Instant decomposition occurred ; cream of tartar was precipitated, and chlorate of soda remained in solution. The whole was permitted to cool, and when quite cold the solution was decanted, evaporated, and crystallized. It is better to employ excess of chlorate of potassa : the proportions which I used were 32 of chlorate and 40 of bitartrate in crystals. The first crop of chlorate of soda generally contains a little bitartrate, but this may easily be separated by cold water, which dissolves the former and leaves the latter. The salt employed for the present inquiry was dissolved in spirit of wine, and afterwards twice recrystallized from distilled water. It was at last crystallized by spontaneous evaporation. The crystals thus obtained were very large. The diagonals of the largest face of many were not less than $\frac{3}{4}$ of an inch in length. They were either right square prisms or right rectangular prisms. I have never obtained them of any other shape. They contain no water of crystallization, and remain unchanged by exposure to the air : they fuse at a temperature a little higher than that required by chlorate of potassa ; and, like this salt, they always undergo a slight decomposition by fusion.

36. Particular attention is required in concentrating the solutions of this salt ; for if the heat be carried too far decomposition will take place. Oxygen in abundance is evolved, and chloride of sodium formed. When this has happened the chlorate is spoilt, for the almost equal solubility of the chlorate and chloride renders it impossible to effect their perfect separation. The criterion by which I judge of the proper strength of a solution, is blowing gently on the surface, and observing whether any crystals are formed ; if so the heat may be removed.

37. The process for decomposition is the same as that employed for chlorate of potassa. In drying the resulting chloride of sodium, care must be taken to avoid a loss by decrepitation.

38. I subjoin the results of four experiments with the calculation to one hundred parts.

Chlorate.	Chloride.	Chlorate.	Chloride.
81.816	44.950	100	54.940
75.010	41.199	100	54.925
116.655	64.067	100	54.920
130.705	71.800	100	54.933

The mean will be very nearly 100 of chlorate to 54.930 of chloride.

39. The chlorate was next converted into nitrate by a process similar to that adopted for the analogous salt of potassa. I performed three experiments, and the following are the particulars.

Chlorate.	Nitrate.	Chlorate.	Nitrate.
110·843	88·536	100	79·875
118·290	94·492	100	79·882
89·112	65·198	100	79·890

The mean will be as 100 of chlorate to 79.882 chloride. And comparing this with the experiments on the conversion of chlorate into chloride,

100 parts of chloride will correspond to 145·425 nitrate,
and 100 parts of nitrate will correspond to 68·762 chloride.

Nitrate of Soda.

40. Was prepared from pure carbonate of soda and nitric acid. The carbonate was obtained pure by repeated crystallizations of common carbonate. It was obtained in fine large crystals, and 200 grains when dried and fused yielded a colourless mass. This mass was then dissolved in distilled water and tested for chlorides, sulphates, lime, iron, &c., but no trace of impurity could be detected. The crystals were dissolved and saturated with pure nitric acid in excess; and the solution evaporated to dryness. The dry salt after heating to expel the excess of acid, was recrystallized three times. The resulting nitrate was quite pure, and was dried previously to use, by fusion in the platina crucible.

41. Its decomposition into chloride of sodium was effected by the same process as that applied to nitrate potassa. In drying the resulting chloride care must be taken to prevent a loss from decrepitation. Fusion must also be avoided, as the salt rapidly sublimes when fused. The hydrochloric acid was added in two portions, and from one ounce to one ounce and a half was sufficient for the quantities of nitrate employed.

42. I subjoin the results of six experiments with the calculations to 100 parts.

Nitrate of Soda.	Chloride Sodium.
1. 56·606	38·926 100 . . . 68·767
2. 59·220	40·731 100 . . . 68·780
3. 5·0316	34·602 100 . . . 68·770
4. 51·794	35·618 100 . . . 68·769
5. 55·250	37·995 100 . . . 68·770
6. 68·430	47·059 100 . . . 68·770

The mean of these results give the following proportions.

100 parts of nitrate soda correspond to 68·771 chloride sodium,
and 100 parts of chloride sodium correspond to 145·410 nitrate.

Chloride Sodium.

This salt was prepared by supersaturating pure carbonate of soda with pure hydrochloric acid. The solution was evaporated to dryness, and the dry salt, after heating to expel the excess of acid, was redissolved and recrystallized several times. The crystals obtained were quite pure, and were fused in the platina crucible to ensure dryness. It was converted into nitrate of soda by the same method as chloride of potassium. The resulting nitrate was fused in the flask. The following are the results of seven experiments. Number 3. was performed upon some chloride of sodium obtained from chlorate, by heating until all the oxygen was expelled. Number 7. was performed upon chloride in powder, dried in the platina crucible by the flame of a spirit lamp. Half an ounce of the nitric acid (27.) was sufficient for all the following experiments.

Chloride.		Nitrate.		Chloride.		Nitrate.
1. 43.758	63.630	as 100 to	145.415
2. 50.454	73.465	, . . .	as 100 to	145.408
3. 38.160	55.492	as 100 to	145.420
4. 48.914	71.112	. . . , .	as 100 to	145.424
5. 56.240	81.778	as 100 to	145.410
6. 58.942	74.021	. . . , .	as 100 to	145.418
7. 99.168	144.210	as 100 to	145.420

whence taking the mean

100 parts of chloride will correspond to 145.416 nitrate,
or 100 parts of nitrate will correspond to 68.768 chloride.

43. The conversion of chloride of sodium into nitrate of soda, affords one of the best and easiest methods for testing the accuracy of the equivalent numbers in general use. According to one series we have 60 as the number for chloride of sodium, and 86 for nitrate; another series gives 53.72, and 85.45 for the same compounds. Now taking these two series as the data of separate calculations, we find, that, according to the former, a hundred grains of chloride should yield 143.333 grains of nitrate; whereas the latter would give 145.504 grains of nitrate from the same quantity of chloride. Here then is a difference of nearly 2.2 grains;—a difference far exceeding any error of manipulation, and plainly indicating that one or other of these series must be incorrect. Upon which series the greater error is chargeable, every chemist may satisfy himself. The decomposition by nitric acid may be readily performed in flasks; and the only requisite for success is purity of materials.

Silver.

44. The object for which the following experiments were made upon this metal has been already stated (5.). The conversion of silver into chloride has been so frequently repeated by the most skilful chemists, that I conceived the better plan would

be to collate their results, and to take the mean as the basis of my calculation. But the discrepancies existing between them, and the objectionable processes which have in many cases been applied, urged me to examine the subject for myself.

45. The purity of the silver employed was very vigorously tested. One hundred and fifty grains were dissolved in pure dilute nitric acid; not a trace of insoluble black matter indicative of gold could be recognised. The nitric solution, being diluted, was precipitated by excess of pure hydrochloric acid; and the supernatant liquor, separated from the precipitate by filtration, was evaporated to dryness. A very minute quantity of solid matter remained; equivalent only to the impurities introduced by the acids and the water. It was examined for copper, lead, and iron, but not the slightest indication of their presence was afforded. The silver was in small pieces, and each piece was sufficient for an experiment.

Conversion into Nitrate.

46. The process for the conversion into nitrate was in all particulars identical to the one described in paragraph number 9. One fluid drachm of the pure nitric acid (27.) diluted with two drachms of distilled water was amply sufficient for the quantities of silver employed. With acid thus diluted the action is very gentle, and, if time be allowed, the whole of the silver may be dissolved without the assistance of heat. During the evaporation of the water and the excess of nitric acid, the receiver flask may be detached without any risk of loss. The dry nitrate was in all cases fused; but particular care is necessary to accomplish this operation successfully, for the salt being in a small cake, is, from the shape of the flask, much thinner at the edges than in the middle; and therefore, unless the heat be cautiously applied, a slight reduction into oxide will happen. This effect becomes evident by the fused nitrate being tinged with black. It only happened in one of the following experiments, and then a very minute black film could be detected on one side of the fused mass. During fusion and cooling, the flasks were always excluded from light.

47. The distilled water employed in these experiments had been twice redistilled in green glass, and four fluid ounces when evaporated left $\cdot 024$ of a grain of solid matter. The quantity used, namely two drachms, would not introduce therefore a thousandth of a grain of impurity.

48. I subjoin the results of six from nine experiments, with the calculations to 100 parts.

	Silver.		Nitrate.		Silver.		Nitrate.
1.	59·087	. . .	93·020	. . .	or as 100 to	. . .	157·430
2.	60·311	. . .	94·952	. . .	or as 100 to	. . .	157·437
3.	51·654	. . .	81·333	. . .	or as 100 to	. . .	157·458
4.	55·734	. . .	86·765	. . .	or as 100 to	. . .	157·440
5.	45·622	. . .	71·827	. . .	or as 100 to	. . .	157·430
6.	64·726	. . .	101·913	. . .	or as 100 to	. . .	157·455

whence, taking the mean, 100 parts of silver correspond to 157·441 of nitrate.

Conversion into Chloride.

49. The quantity of chloride resulting from a known weight of silver was determined as follows. To each of the fused nitrates from several of the foregoing experiments (48.), half a fluid ounce of distilled water (47.) was added, and the salt dissolved with the assistance of a gentle heat. The solution being slightly acidulated with nitric acid, was precipitated by an excess of pure hydrochloric acid, amounting to half an ounce. These operations were performed without removal from the flask. The precipitated chloride, notwithstanding constant agitation during the addition of the hydrochloric acid, forms into a cake, and lest this should retain any undecomposed nitrate of silver, a glass rod of a dark green colour was introduced and the mass broken up. The rod, on removal from the flask, was always examined with a lens to see whether any chloride had adhered. The flask was next placed upon a heated sand bath, and the water and excess of acid cautiously expelled. The resulting chloride was beautifully white, and was always fused in the flask. During this operation, and while cooling, light was carefully excluded.

50. In the Philosophical Transactions for 1833, the late and much-lamented Dr. TURNER has stated that chloride of silver may be dried perfectly and without the risk of decomposition at a temperature of 300° FAHR.; but he adds that even after this a slight loss occurs during fusion. With the latter part of these remarks my observations accord. In several experiments in which the chloride has been dried for a considerable time with a spirit lamp, guarding carefully against fusion, I have found that thus dried it always decreased slightly in weight by fusion, amounting to about .006 of a grain for 70 grains. Dr. TURNER attributed this loss to a slight decomposition. I have repeatedly tried to satisfy myself on this point, but have hitherto been unsuccessful. I have never seen any evidence of decomposition.

51. In five experiments performed as already stated, I obtained the following results.

Silver.	Chloride.	Silver.	Chloride.
1. 59.087 . . .	78.489 . . .	or 100 to . . .	132.836
2. 60.311 . . .	80.117 . . .	or 100 to . . .	132.840
3. 51.654 . . .	68.612 . . .	or 100 to . . .	132.830
4. 55.734 . . .	74.037 . . .	or 100 to . . .	132.840
5. 64.726 . . .	85.982 . . .	or 100 to . . .	132.840

52. Again, in two additional experiments I dissolved the silver in a sufficient quantity of dilute nitric acid, and precipitated at once with hydrochloric acid, without evaporating and procuring the nitrate. These are the particulars of the experiments.

Silver.	Chloride.	Silver.	Chloride.
57.882	76.884	100	132.830
51.380	68.252	100	132.838

Taking the mean of the seven experiments, 100 parts of silver will correspond to 132.836 of chloride.

53. The mean of three experiments, described by Dr. TURNER in the Philosophical Transactions for 1829, gives the ratio of 100 of silver to 132·835 of chloride. The following table, extracted from Professor BRANDE's Manual of Chemistry, will show the results of different experimenters upon the same subject.

Dr. THOMPSON.	100 of silver to 133·333 of chloride.
ROSE	100 of silver to 133·014 of chloride.
BERZELIUS	100 of silver to 132·736 of chloride.
GAY LUSSAC	100 of silver to 132·890 of chloride.
MARCET and DAVY	100 of silver to 132·450 of chloride.

54. From the five experiments on the chloride, we can also ascertain the ratio of nitrate of silver to chloride. For as the silver employed had been previously converted into nitrate, we can, by comparing the mean result from the nitrates with that from the chloride, obtain the ratio required. Thus every 100 parts of silver correspond to 132·836 of chloride and to 157·441 of nitrate; whence,

100 of chloride will correspond to 118·523 nitrate,
and 100 of nitrate will correspond to 84·372 chloride.

Nitrate Silver.

55. That 100 parts of nitrate to 84·372 of chloride is near the truth, the following experiments on the crystallized nitrate satisfactorily confirm. The nitrate of silver was obtained from pure commercial silver by solution in nitric acid and crystallizing. After three crystallizations it was obtained in fine bold crystals, and was quite pure. Its perfect dryness was ensured by fusion in a small glass tube. To convert it into chloride, the same process and precautions were adopted as have already been described. The chloride was always fused.

56. I subjoin the results of five experiments.

Nitrate.	Chloride.	Nitrate.	Chloride.
93·452	78·847	100	84·370
115·414	97·395	100	84·388
65·500	55·267	100	84·377
93·034	78·490	100	84·367
108·645	91·664	100	84·370

The mean of these experiments will be

100 of chloride to 118·520 nitrate,
and 100 of nitrate to 84·374 chloride.

57. Dr. TURNER, in the Philosophical Transactions for 1829, gives the details of two experiments upon the conversion of nitrate of silver into chloride. According to one, 100 parts of nitrate correspond to 84·357 of chloride; and to the other, 100 to 84·389. The mean will be 100 to 84·373. The close accordance of the above results

not only proves the correctness of the experiments, but also the purity of the materials.

58. It now remains to determine from the foregoing experimental data, the equivalent numbers of the several compounds described, and of the elementary bodies of which these compounds are constituted. For the convenience of reference, I have arranged the results in a tabular form, and have included the results corresponding to the two series of numbers in general use in this country. I have taken the liberty to name them according to their respective authors.

	Calculated according to DR. THOMPSON.	Calculated according to DR. TURNER.	According to the foregoing experiments.
100 parts of chlorate of potassa yield of chloride....	61.290	60.838	60.825
100 parts of chlorate of potassa yield of nitrate ...	82.259	82.646	82.500
100 parts of chloride of potassium yield of nitrate....	134.210	135.845	135.636
100 parts of nitrate of potassa yield of chloride.....	74.510	73.613	73.726
100 parts of chlorate of soda yield of chloride	55.555	55.022	54.930
100 parts of chlorate of soda yield of nitrate.....	79.630	81.942	79.882
100 parts of chloride of sodium yield of nitrate.....	143.333	145.504	145.414
100 parts of nitrate of soda yield of chloride.....	69.767	68.666	68.771
100 parts of silver yield of nitrate.....	156.363	157.546	157.441
100 parts of silver yield of chloride	133.333	132.796	132.837
100 parts of nitrate of silver yield of chloride	85.272	84.290	84.374
100 parts of chloride of silver yield of nitrate....	117.808	118.637	118.520

59. Of the six elementary substances included in the above compounds, there is only one upon the number of which chemists are agreed. That is oxygen. Upon a scale in which hydrogen is considered as unity, oxygen is stated to be eight; and as this number is generally employed in this country, we may adopt it as the basis of the calculations in the present inquiry. Should it be proved erroneous by future investigations, the numbers, presently deduced, must undergo a proportionate alteration. Remembering, therefore, that I have merely assumed the number eight for oxygen to be correct, we may proceed according to the method already detailed (5.) to ascertain the several equivalents.

60. Chloride of Potassium. According to the preceding table 100 parts of chlorate of potassa correspond to 60.825 of chloride, and therefore the same quantity of chlorate will contain 39.175 oxygen. But in every proportional of chlorate, there are admitted to be six proportionals of oxygen; whence as $39.175 : 60.825 :: 48 :$ to the equivalent of chloride of potassium. By performing the operation we obtain the number 74.527. Chlorate of potassa will therefore be $74.527 + 48 = 122.527$. Nitrate of potassa is determined by the ratio which chloride bears to nitrate, thus according to the table 100 of chloride correspond to 135.636 of nitrate; and therefore as $100 : 135.636 :: 74.527 : 101.087$, which will be the equivalent of nitre. Moreover from what has been stated (5.) we learn, that 122.527, the equivalent of chlorate, minus 101.087 the equivalent of nitrate, equals the difference between chlorine, and nitrogen, namely 21.440;—and also that 101.087, minus 74.527 the number for

chloride, is the difference between one proportional of nitrogen plus six of oxygen minus chlorine: namely 26·560.

61. By performing the same method of calculation with the results from the salts of sodium, we have as follows:

Chloride of sodium	58.500
Chlorate of soda	106.500
Nitrate of soda	85.068
Chlorine—nitrogen	21.432
Nitrogen + 6 oxygen—chlorine	26.568

The close accordance of these latter differences with those from the salts of potassium cannot fail, I think, to inspire confidence in the accuracy of the experiments.

62. From these differences we may readily determine the numbers for the salts of silver as well as those for chlorine and nitrogen. Thus, according to the table, 132·837 of chloride of silver correspond to 157·441 of nitrate: the difference being 24·604. But we have ascertained that the difference between a nitrate and a chloride is 26·565, and therefore as 24·604 : 157·441 or 132·837 :: 26·565 : to the equivalent of chloride or of nitrate of silver. Whence the nitrate equals 169·989 and the chloride 143·424; and as 132·837 of chloride contain 100 of silver, therefore the number for silver is 107·970.

63. Nitrogen will be 14·02 and chlorine 35·454. Potassium therefore is 39·073, and sodium 23·046.

64. For the convenience of reference I have subjoined the numbers of these elementary bodies in the following table; with the numbers given by the two distinguished chemists whose names I have had occasion to mention.

	THOMPSON.	TURNER.	PENNY.
Oxygen	8	8	8
Chlorine	36	35.42	35.45
Nitrogen	14	14.15	14.02
Potassium	40	39.15	39.08
Sodium	24	23.3	23.05
Silver	110	108.0	107.97

65. These researches corroborate the conclusions to which Dr. TURNER was led by his experimental inquiries, published in the Philosophical Transactions for 1833. They show that the estimates in general use among British chemists are not the strict representatives of chemical truth, founded on experiment; and that the favourite hypothesis, of all equivalents being simple multiples of hydrogen, is no longer tenable. My estimates of chlorine and silver correspond very closely to those of Dr. TURNER. His number for nitrogen was deduced from experiments on the nitrates of silver, lead, and baryta. He obtained the numbers 14·09, 14·17, 14·2, and he adopted 14·15 as the mean. I have carefully re-examined my experiments, but I cannot discover

anything to justify an alteration of the number 14.02. The experiments upon the conversion of silver into nitrate have satisfied me that 14.15 for nitrogen is inaccurate; for by reference to the table in page 31, it will be seen that according to this number I should have obtained 157.546 of nitrate from 100 of silver, whereas I obtained 157.441. The difference, namely, 0.1, is too high to be referable to errors of manipulation, considering the simplicity of the process employed. Dr. TURNER's numbers for potassium and sodium are not founded upon any experiments of his own, but are extracted from BERZELIUS's Tables of Equivalents.

66. In conclusion, I may mention the several additional subjects which the present inquiry has elicited for investigation. I have extended the decomposition of nitrates into chlorides, and chlorides into nitrates, to the salts of baryta, lime, strontia, manganese, and lead; but whether these salts are applicable to the determination of equivalent numbers, must be decided by future experiments.

67. I have also satisfied myself, that the same method of investigation may be applied to several iodates and iodides, bromates and bromides. They are converted into chlorides by hydrochloric acid; and the iodides and bromides may be converted into nitrates by nitric acid. These decompositions afford excellent means of determining the equivalents of iodine and bromine, and of corroborating the experiments already described upon the nitrates and chlorides. For suppose that two equal quantities of pure iodate or bromate of potassa are converted into chloride and nitrate, it is obvious that the quantities of these resulting salts should bear the same ratio to each other as that established in the present paper. The same ratio should result from the iodides and bromides, if the experiments be correctly performed. Opportunity, however, will not permit me at present to complete the experiments undertaken upon these salts. The special care required in the preparation of the materials, the number of experiments to be performed, and the extreme delicacy necessary to attain truth, would occupy so much time, that I have deemed it better to communicate the results already obtained, than to wait for the completion of the whole. Moreover the details would far exceed the just limits of a single communication.

68. I have likewise examined the action of nitric acid upon chlorates and iodates, and have obtained some novel and interesting results. The process so frequently referred to has also enabled me to make some satisfactory experiments upon the conversion of carbonate of soda into nitrate and chloride, and to obtain some important evidence respecting the equivalent of carbon.

69. As soon as opportunity will permit me to resume and complete these several investigations, I shall do myself the honour of communicating them to the Royal Society.

APOTHECARIES' HALL,
January 10th, 1839.

